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The importance of network structure in high- k dielectrics: LaAlO_3 , Pr_2O_3 , and Ta_2O_5

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Measurements of the dielectric constant of amorphous and crystalline Pr_2O_3 are reported. The high value ~ 25 for the polycrystalline phase is discussed in terms of the network structure and comparison is made with heavy rare-earth oxide values. The specific cases of LaAlO_3 and Ta_2O_5 are also discussed and the role of network structure evidenced and elucidated. A potential route to finding high k materials suitable for microelectronics applications is suggested. © 2005 American Institute of Physics. [DOI: 10.1063/1.2012513]

I. INTRODUCTION

Thin-film high dielectric insulators remain a potential “show stopper” for the evolution of silicon-based microelectronics in the generations to come as outlined in the semiconductor industries roadmap.¹ Specifically, a dielectric constant (k) ~ 25 is required to satisfy the requirements for metal-oxide-semiconductor field-effect transistor (MOSFET) gate dielectrics leading out to years beyond 2010. Similar or larger values are required for dielectrics used in embedded dynamic random access memory (DRAM) cells and radio-frequency (RF) coupling capacitors. The material must also respond positively to a series of other demands relating to such effects as lack of interactivity with the Si substrate, low leakage currents, low interface state density, high electrical barriers against charge injection, etc.² To date, no suitable material has been proposed although a host of different mixed oxides has been examined.

One of the materials which appeared to potentially have great promise as high- k dielectric replacement for SiO_2 was LaAlO_3 . It has a wide electronic band gap of ~ 6 eV, an acceptable band offset³ (~ 1 eV), dielectric constant of ~ 26 in the crystalline state, and projected thermodynamic stability⁴ in the presence of Si. However, it turns out that LaAlO_3 is not stable at high temperature in contact with Si (Ref. 5) and that the amorphous phase produced during a deposition sequence⁶ has a dielectric constant of only 13. As a consequence of the high-temperature reactivity, the crystalline phase with its higher k value cannot be attained by recrystallization of the amorphous material, at least, when the film is deposited on Si. Though the use of LaAlO_3 in advanced Si technology is unlikely on the basis of the information advanced, the significantly different dielectric constant values between the amorphous and crystalline phases are in-

triguing. They lead us to suggest that one might, perhaps, learn something significant from the dielectric constant measurements which have been made. The focus of this paper will therefore be an understanding of the intimate relationship between the dielectric constant and the atomic structure of the dielectric network. The need to integrate this understanding into any considerations used when trying to determine which alloyed oxide systems will potentially resolve the “high- k dilemma” is assumed to be essential.

The generalized importance of the atomic network in determining the dielectric constant in simple binary and multiple oxide systems will be discussed in the following for the rare-earth (RE) oxide system RE_2O_3 , Ta_2O_5 , and LaAlO_3 . In order to include the RE_2O_3 system, we have performed measurements on Pr_2O_3 alloys, these will be described in the first instance.

II. EXPERIMENT

In order to resolve apparent inconsistencies in the published data on Pr_2O_3 we have manufactured thin films of this material and performed electrical and optical measurements on it. The 4" Si (100) wafers were deoxidized in HF acid and blown dry to leave a passivated, native oxide-free surface prior to deposition of the Pr_2O_3 . Using an electron-beam evaporator together with Pr_6O_{11} as the source and a partial pressure of 2.5×10^{-5} torr of O_2 films of ~ 110 nm of Pr_2O_3 were deposited at room temperature. Single wavelength ellipsometry ($\lambda = 632.8$ nm) indicated that the refractive index of the deposited film was 1.80 ± 0.005 . Some films were annealed in flowing O_2 at 400°C following deposition and for these the refractive index was 2.025 ± 0.005 . Al dots, 1 mm in diameter, were evaporated onto the surface of the oxide films through a shadow mask to form metal-oxide-semiconductor (MOS) capacitors. The capacitance/voltage curves for these capacitors were then measured at a frequency of 100 kHz using a Keithley 590 system. From the

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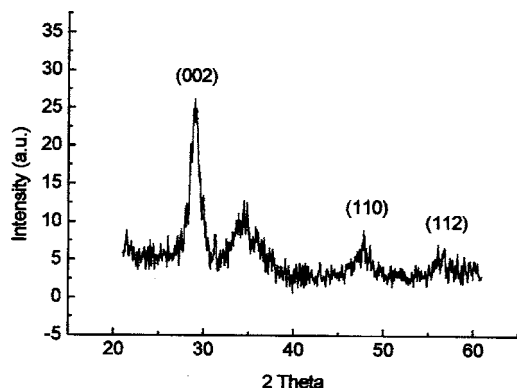


FIG. 1. The x-ray-diffraction plot for the recrystallized samples of Pr_2O_3 annealed in O_2 at 400°C . The plots have been smoothed to accentuate the diffraction peaks.

capacitance plots in strong accumulation we determined the dielectric constant of the films to be 16 ± 1 (as-deposited samples) and 25.4 ± 0.7 (annealed samples).

Standard x-ray-diffraction measurements were made using $\text{Cu K}\alpha$ radiation, the diffraction intensity versus 2θ curve is shown in Fig. 1 for the annealed sample. The curve for the as-deposited sample showed no sharp peaks consistent with it being amorphous. The recrystallized sample peaks at 29.2° , 47.55° , and 56.55° concur with those obtained by other authors⁷ and identified as due to the hexagonal phase of Pr_2O_3 . Glancing incidence x-ray reflectivity was used to ascertain the density of the as-deposited and recrystallized films. The reflectivity was measured using a Philips X'pert double crystal diffractometer with $\text{Cu K}\alpha$ radiation and a 0.45-mm receiving slit. The experimental data is shown in Figs. 2(a) (amorphous, as deposited) and 2(b) (recrystallized at 400°C in flowing O_2) together with the fits obtained using the WINGIXA software supplied by the PANalytical company. Note that the fit curves are displaced vertically with respect to the experimental curves in order to facilitate judgement of the quality of the fits. The fits yield the values of 6.42 ± 0.2 and $7.08 \pm 0.2 \text{ g cm}^{-3}$ for the densities in the as-deposited and annealed samples, respectively.

III. DISCUSSION

In order to discuss the importance of the network in determining the dielectric constant we will throughout appeal to the classical Clausius-Mosotti formula which relates the dielectric constant to the molecular polarizability α_D and the molecular volume V_m ,

$$(k - 1)/(k + 2) = (4\pi/3)\alpha_D/V_m. \quad (1)$$

For the purposes of the discussion here we will not make use of the oxide additivity rule form of Eq. (1) appropriate to mixed oxide systems.⁸

A. The RE_2O_3 system

Though the RE_2O_3 compounds are in general hygroscopic and therefore of little use in standard technological applications, a study of the variation of the dielectric constant with RE ion is informative. Various authors have measured the dielectric constants in RE_2O_3 binary oxides and

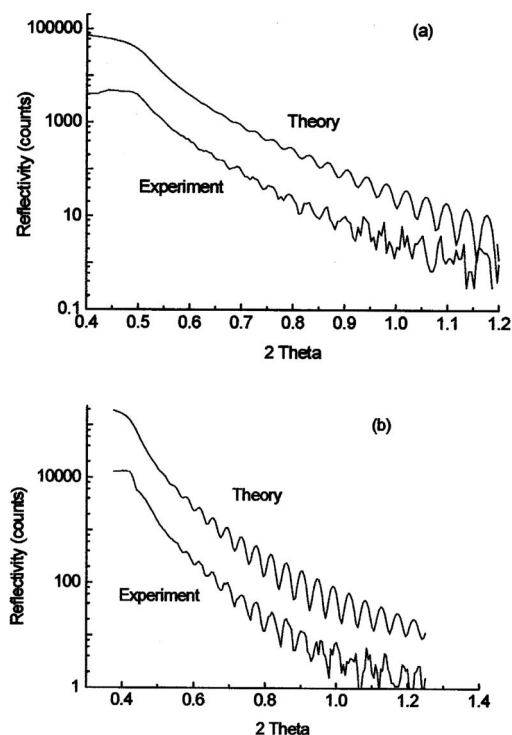


FIG. 2. Glancing incidence x-ray scattering data for Pr_2O_3 films (a) amorphous and (b) recrystallized. In both plots the fit curves are shown simply displaced vertically in order to give a clearer indication of the quality of the overall fit to the experimental curves.

their values are given in Table I. There is sometimes a wide disparity which may arise perhaps due to uncertainty as to the state of the material (amorphous or crystalline) or because during the experiments an SiO_2 layer has formed at the dielectric/semiconductor interface which has a net effect of lowering the overall effective dielectric constant. The most reliable data appears to be that on the crystalline RE_2O_3 films grown on Si since here it is most likely that an amorphous SiO_2 barrier layer has not formed. As a general rule the higher dielectric constant values are associated with the crystalline phases and this is because the molecular volume is usually smaller for these denser polymorphs. The particularly interesting example in point is the case of Pr_2O_3 where we have found that $k \sim 16$ for the amorphous state and 25.4 for the crystallized, hexagonal phase. The latter value is consistent with that obtained by other workers for recrystallized films,¹³ the structure of these films is polycrystalline hexagonal. An even higher value for Pr_2O_3 of 31 has been observed for epitaxially grown film on the Si (100) face. Note, however, that in this case the structure is cubic, not the more usual hexagonal.

What might seem at first inconsistent is that the dielectric constants measured for the crystalline, lighter rare-earth oxides La_2O_3 , and Pr_2O_3 are significantly larger than in the heavier, crystalline rare-earth case (as evidenced in Table I). It is important to note from Eq. (1) that the two parameters are of importance in determining k , the molecular volume V_m and the molecular polarizability α_D . In Fig. 3 we show the molecular volume values as a function of rare-earth ion for the rare-earth oxide series as determined from the published

TABLE I. Measured values of the dielectric constant k molecular volume (in units of 10^{-24} cm³) and molecular polarizability (in units of 10^{-24} cm³) in RE₂O₃ compounds.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
k value	22 ^a	21.2 ^b	15.5 ^b	13.9 ^b		11.4 ^c	13.7 ^b	12.9 ^b	12.9 ^b	12.5 ^b	12.5 ^b	12.6 ^b	13.4 ^b	12.5 ^b	
	20 ^d		25 ^e	12.9 ^f		46 ^g		13.9 ^c		14.3 ^c					12 ^h
	27 ⁱ		16 ^j					14 ^f							
			25.4 ^j												
			31 ^k												
			15 ^c												
Molecular volume							79.8	78.7	76.6	75.7	74.3	72.9	72.4	70.6	69.6
α_D	83.1		79.4	77.2		76.2	78.6	81.2	76.8	79.3	74.6	73.5	74.5	70.7	70.2
	17.1		16.85			17.1	15.29	15.5	14.6	14.9	14.1	13.9	13.9	13.6	13.2

^aReference 9.^bReference 12.^cReference 15.^dReference 10.^eReference 13.^fReference 17.^gReference 16.^hReference 18.ⁱReference 11.^jPresent work.^kReference 14.

density measurements.¹⁹ We see that for ions lighter than Eu there appears to be a finite decrease in molecular volume and this step correlates directly with a structural change. In fact the heavier rare-earth oxides are cubic whereas the lighter ones are hexagonal.²⁰ Straightforward inspection of Eq. (1) indicates that a reduction in molecular volume will lead directly to an increase in k if the molecular polarizability remains constant or indeed increases. It is important to determine the molecular polarizabilities in these compounds and to observe the consequences, if any, of the steplike volume modification. Using the crystalline k data and molecular volumes from Table I, we calculate, using Eq. (1), the molecular polarizabilities which are also presented in Table I and shown graphically in Fig. 4(a). In Fig. 4(a) we include the data on rare-earth garnets, RE₃Ga₅O₁₂ is taken from Ref. 21 a monotonic decrease in α occurs as one crosses the periodic table from light to heavy REs. There appears to be no discontinuity in the variation of α as one crosses the series. If the large increase in dielectric constant in the lighter REs as compared to the heavier ones would have been attributed to a variation in α_D alone, then a nonmonotonic variation would have resulted rather similar to the nonmonotonic variation of the molecular volume shown in Fig. 3. The comparatively

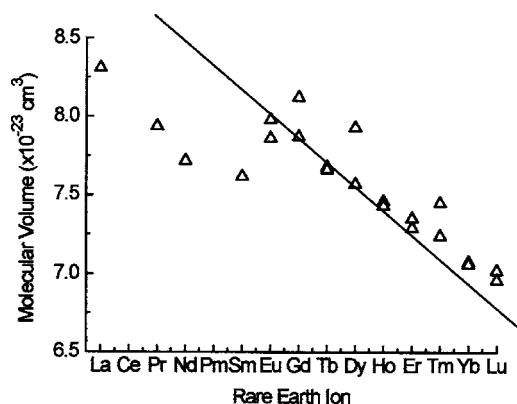


FIG. 3. A plot of the molecular volume as a function of rare-earth ion in the series RE₂O₃. The lighter RE's below Eu are expected to form the hexagonal close-packed phase while the heavier RE's form the cubic phase.

similar behavior of α_D in the oxide and garnet series shown in Fig. 4(a) confirms our interpretation of the variation of k with ion in the RE series, namely, that the jump in dielectric constant results primarily from a change in the volume of the RE₂O₃ network due to a phase change.

The data for RE₂O₃ and RE garnet compounds shown in Fig. 4(a) suggest a monotonic decrease in α_D with RE ion. We shall approximate

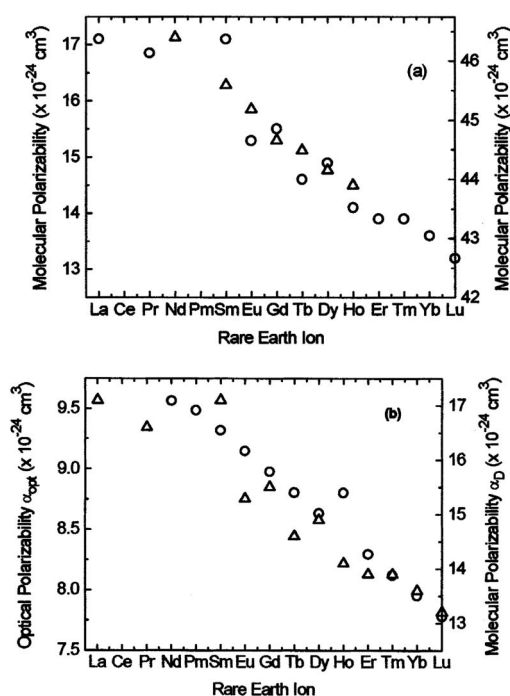


FIG. 4. (a) The variation of the molecular polarizability in (○) the RE₂O₃ compounds deduced from the crystalline phase dielectric constant values shown in Table I, left-hand scale and (△) for the RE garnets and right-hand scale for the RE₃Ga₅O₁₂. (b) Variation of the optical polarizability α_{opt} for the crystalline RE₂O₃ compounds, from Ref. 23 (○) (left-hand scale) and the low-frequency molecular polarizability calculated from the measured dielectric constant (△) (right-hand scale).

$$(3V_m/4\pi)(k-1)/(k+2) = \alpha_D$$

$$= 2\alpha_{\text{RE}^{3+}} + 3\alpha_{\text{O}^{2-}} + F_o^{-1}(Z-Z')^2, \quad (2)$$

where the term $F_o^{-1}(Z-Z')^2$ is defined in Ref. 22 and is related to the relative displacement of the RE and O ions in the network. We have assumed an additivity model for the ionic polarizabilities and that they are related to the material refractive indices n through

$$(3V_m/4\pi)(n-1)/(n+2) = \alpha_{\text{opt}} = 2\alpha_{\text{RE}^{3+}} + 3\alpha_{\text{O}^{2-}}. \quad (3)$$

Values for the optical frequency polarizability in the RE_2O_3 series have been determined²³ and they are shown in Fig. 4(b) together with the values of the low-frequency polarizability determined from the dielectric constant using Eq. (2). There is clearly a reduction in polarizability as one crosses the RE_2O_3 series from light to heavy rare earths although the variation in the optical polarizability component is a factor of 2 smaller than that of the low-frequency polarizability. Comparing Eqs. (2) and (3) this suggests that some variation in the term related to the relative displacement of the composite ions may also be occurring. The observed monotonic decrease of the effective polarizability across the RE series is apparently, however, supported both on the basis of the optical and low-frequency measurements. Calculations of α_{opt} may be made using the published individual ionic components²⁴ ($\alpha_{\text{RE}^{3+}}$ and $\alpha_{\text{O}^{2-}}$) for the closed-shell configurations of the individual ions. Though the absolute magnitude is in disagreement with experiment, again the general trend of a decrease in polarizability across the series is anticipated.

The behavior of the experimentally observed dielectric constant across the crystalline RE_2O_3 series can therefore be entirely expected in terms of the structure of the oxide network and the variation of the ionic contributions with closed-shell configuration of the RE ions. Before leaving this section we return to our single point data on amorphous Pr_2O_3 where we found that $k \sim 16$ and the density $\rho \sim 6.4 \text{ g cm}^{-3}$. Using these values we calculate $V_m = 85.6 \times 10^{-24} \text{ cm}^3$ and $\alpha_{\text{amorphous}} = 17 \times 10^{-24} \text{ cm}^3$ to be compared with $V_m = 78.1 \times 10^{-24} \text{ cm}^3$ and $\alpha_{\text{hexagonal}} = 16.6 \times 10^{-24} \text{ cm}^3$ for the hexagonal crystalline phase. These results lead us to conclude that the polarizability is relatively network insensitive for Pr_2O_3 and that the primary driver in varying the dielectric constant is the density of the network through its atomic structure.

B. The Ta_2O_5 system

The success in understanding the behavior of the dielectric constant in the RE_2O_3 series in terms of variation in the structure of the network leads us to examine another material where potentially surprising results are obtained, specifically Ta_2O_5 . In amorphous Ta_2O_5 the measured²⁵ dielectric constant is typically 25. At relatively low annealing temperatures ($>700^\circ\text{C}$) orthorhombic²⁶ and hexagonal²⁶ crystalline phases have been stabilized. In the former case increased dielectric constants varying from 30 to 50 have been reported^{27–29} whereas in the latter (hexagonal) the dielectric constant is reported between 55 and 64.³⁰ Note that the

TABLE II. Density, molecular volume, measured dielectric constant, and molecular polarizability for various phases of Ta_2O_5 .

Phase	Density g cm^{-3}	Molecular volume $\times 10^{-24} \text{ cm}^3$	Dielectric constant	Molecular polarizability $\times 10^{-24} \text{ cm}^3$
Amorphous	8.10	90.60	25	19.2
Orthorhombic	8.24	89.03	45–52	19.9–20.1
Hexagonal	8.32	88.18	55–64	19.9–20.1
Monoclinic	8.48	86.51	126–189	20.2–20.3

orthorhombic phase appears to be the most stable form. Of particular note is the data^{31,32} concerning the effect of substitution of Ta_2O_5 by small quantities of TiO_2 [particularly $0.92(\text{Ta}_2\text{O}_5) 0.08(\text{TiO}_2)$] $-k$ values of 126 and 189 have been reported for these mixed oxide compositions. We note that the structure of the Ta_2O_5 network in the titania stabilized network is monoclinic as it is with other stabilizing binary oxides.³³ However, not all binary oxide additions stabilize the monoclinic form, many stabilize the orthorhombic phase^{28,34} where significantly lower dielectric constants are observed as expected.

In Table II we summarize the relevant parameters for the different phases of Ta_2O_5 which enable us to calculate the molecular polarizabilities and molecular volumes. Equation (1) has been used together with the measured dielectric constants and known molecular volumes to deduce the molecular polarizability for each phase and we remark that over the range of phases studied, whereas the molecular volume decreases by 4.5%, the molecular polarizability increases by 5.7%. The sense of these changes is such that α/V_m increases by $\sim 10\%$. The effect of this change is best seen pictorially in Fig. 5 where we plot k as a function of α/V_m as calculated from Eq. (1). The dramatic increase in k with α/V_m clearly explains why such large k values are observed.

We apply the additivity rule $\alpha_{\text{opt}} = 2\alpha_{\text{RE}^{3+}} + 3\alpha_{\text{O}^{2-}}$ together with the ionic polarizabilities for Ta and O from Ref. 24 $\alpha_{\text{opt}}(\text{Ta}^{5+}) = 4.73 \times 10^{-24} \text{ cm}^3$, $\alpha_{\text{opt}}(\text{O}^{2-}) = 2.01 \times 10^{-24} \text{ cm}^3$, and determine $\alpha_{\text{opt}}(\text{Ta}_2\text{O}_5) = 19.51 \times 10^{-24} \text{ cm}^3$. This value is actually within 1.6% of the value of α_D determined for amorphous Ta_2O_5 as shown in Table II. However,

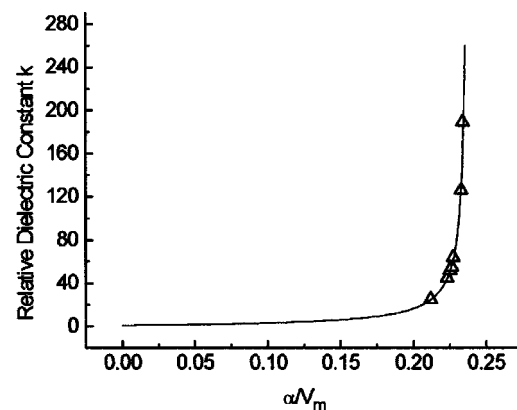


FIG. 5. Variation of the dielectric constant as a function of the ratio of the molecular polarizability to the molecular volume (α/V_m) as anticipated from Eq. (1). (Δ) the values of k measured experimentally which enable deduction of the respective α/V_m values.

using Eq. (3) together with the measured refractive index of 2.1 we obtain $\alpha_{\text{opt}}(\text{Ta}_2\text{O}_5) = 11.3 \times 10^{-24} \text{ cm}^3$, this discrepancy is in the same sense and of similar magnitude (almost a factor of 2) as that observed when treating the case of RE_2O_3 compounds above. It would appear that the calculated ionic polarizabilities²⁴ are almost a factor of 2 too large.

C. The LaAlO_3 system

As mentioned above, the dielectric constant of amorphous LaAlO_3 is ~ 13 while it is 26 for the crystalline phase.⁶ It has been determined that $V_m \sim 84.5 \pm 6 \times 10^{-24} \text{ cm}^3$ for the amorphous phase and $54.5 \times 10^{-24} \text{ cm}^3$ for the crystalline state. We note that $V_m(\text{crystalline})/V_m(\text{amorphous})$ is 64.5% whereas for the Pr_2O_3 and Ta_2O_5 cases we obtained $V_m(\text{hexagonal})/V_m(\text{amorphous}) = 91.6\%$ and $V_m(\text{monoclinic})/V_m(\text{amorphous}) = 95.5\%$, respectively, the latter variations are substantially less than that observed for LaAlO_3 . It has been underlined⁶ that there is evidence in LaAlO_3 for a significant change in atomic coordination number when comparing the amorphous and crystalline states and this would account for dramatic changes in apparent density.

The resultant molecular polarizability values are $\alpha_D(\text{amorphous}) = 16.1 \pm 1.1 \times 10^{-24} \text{ cm}^3$ and $\alpha_D(\text{crystalline}) = 11.6 \times 10^{-24} \text{ cm}^3$. Again using the ionic polarizabilities determined in Ref. 24 we predict $\alpha_{\text{opt}}(\text{LaAlO}_3) = 12.9 \times 10^{-24} \text{ cm}^3$. This value is “relatively” close to the crystalline α_D value but substantially different from the amorphous value. Furthermore, using the experimental value³⁴ for n we deduce $\alpha_{\text{opt}}(\text{LaAlO}_3) = 6.54 \times 10^{-24} \text{ cm}^3$ which yet again differs from the calculated value²⁴ by a factor of nearly 2.

If we compare the variation of α_D with V_m for the various materials we have studied, no systematic behavior emerges. In the case of LaAlO_3 , α_D increases with V_m which is the opposite of what is found for Ta_2O_5 (Table II). However, in the case of Pr_2O_3 , α_D again increases with increasing V_m although the variation is small. Comparison of the values of α_{opt} calculated from the published ion polarizability data and the values of α_D deduced from the experiment give a guide as to the behavior of the polarizability in the RE_2O_3 system and, surprisingly, the absolute values are similar. This is, however, inconsistent with the fact that such calculations neglect the ion displacement polarizability term. Furthermore, the actual α_{opt} values determined from optical experiments are overestimated by the calculation. More detailed measurement and analysis are required to elucidate this behavior.

IV. CONCLUSIONS

We have endeavored to analyze the behavior of the dielectric constant in the amorphous and crystalline alloys of LaAlO_3 , Ta_2O_5 , and RE_2O_3 . Though the behavior of the molecular polarizability turns out to be complicated, the overall importance of the network structure in determining the di-

electric constant is clearly underlined. Specifically, very large values observed in the case of Ta_2O_5 can be directly related to the formation of a dense crystalline phase which is, interestingly, stabilized by the addition of relatively small quantities of secondary binary oxides. This observation strongly suggests an approach which might be exploited in the dilemma to find alternative high- k materials for microelectronics applications. Namely, to look for metastable, high-density phases of dielectrics which already have relatively high dielectric constant values in their equilibrium phases.

¹ITRS roadmap available on: <http://public.itrs.net/Files/2001ITRS>

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